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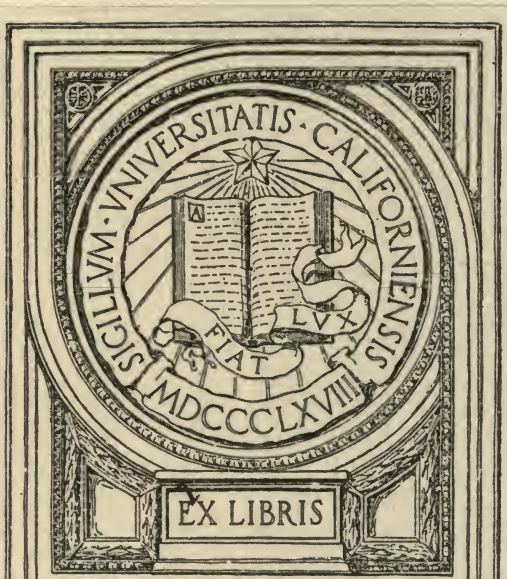

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SCIENCE BULLETIN, No. 4.

September, 1911.

A Modification of Marsh's Apparatus for the Detection of Arsenic.

By

LIONEL COHEN,

Chemist's Branch.

Workers in the respective branches of Economic Science covered by this series of Science Bulletins will receive such of them as may be of use in their special branches of study upon application to the Under Secretary, Department of Agriculture, Sydney.

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A Modification of Marsh's Apparatus for the Detection of Arsenic.

LIONEL COHEN, Chemist's Branch.

THOSE who have worked with Marsh's apparatus for the detection of arsenic are aware of the difficulty of obtaining a prolonged and uniform current of hydrogen, and have sometimes noticed how, when the stream becomes very sluggish, a series of minute explosions occurs in the heated combustion tube, resulting in the formation of dew or water drops therein. Furthermore, that *sine qua non* of the original apparatus, arsenic-free zinc, is not always easily obtainable in quantity.

Many useful suggestions with a view to improvement have been made by chemists from time to time, the chief of these being :—(1) The attachment of a reservoir of hydrogen to obtain a stronger flow of gas; (2) the addition of a copper or platinum salt to very pure samples of zinc in order to promote galvanic action; and (3) the substitution of magnesium for the latter metal.

The standard electrolytic apparatus, of course, possesses great advantages over the zinc method, but is impracticable in many laboratories owing to lack of suitable source of current, &c. The initial expense is also rather high. The interposition of a hydrogen gasometer or reservoir postulates a supply of arsenic-free gas.

Where quantities of pure zinc are not available, the use of platinum or copper salts merely expedites the consumption of the small amount on hand. Magnesium is expensive; its reaction with dilute acid is also very violent, and if sufficiently strong acid is used to promote a stream of gas of requisite volume, so much heat is evolved as to cause the solution to boil and generate large quantities of steam.

The use of aluminium is open to the same objection; moreover, it generally contains silicon as an impurity, resulting in a deposit of silica in the heated tube, through decomposition of the silicon hydride.

The following modification of Marsh's apparatus, as used by the author, is described for the information of those who wish to avoid some of the disadvantages attending the older forms:—

Impure hydrogen, generated from dilute sulphuric acid and ordinary granulated commercial zinc, is purified by passing through a neutral aqueous solution of silver nitrate, which combines with the AsH_3 with reduction to metallic silver. It then passes through a mixture of the suspected liquid with dilute sulphuric acid, in contact with a small quantity of pure arsenic-free zinc, or a bundle of magnesium wire (in which latter case the solution must contain only very little free acid, so as to avoid much heating), and carries over the small quantity of hydrogen thus produced, with the AsH_3 resulting from the reduction of any arsenic present in the suspected matter. The combined gases, after drying, are tested in the usual way.

The arrangement described and figured below will be found a simple one, and has given every satisfaction in the author's hands.

The hydrogen-generating vessel (*a*) is an ordinary 40-oz. flask, fitted with a safety thistle funnel (*g*), with side tube, and charged with about 4 oz. commercial granulated zinc. The side tube is connected by a small piece of rubber tubing to a bent glass tube passing through a cork fitting into the neck of a small conical filtering flask (*b*), containing about 200 cc. of a solution of silver nitrate in distilled water (about 5 per cent.). The side tube of this flask connects with the inlet tube of a second similar filtering flask, containing a further quantity of the same solution. The hydrogen issuing from the second $AgNO_3$ solution will be found perfectly free from arsenic.

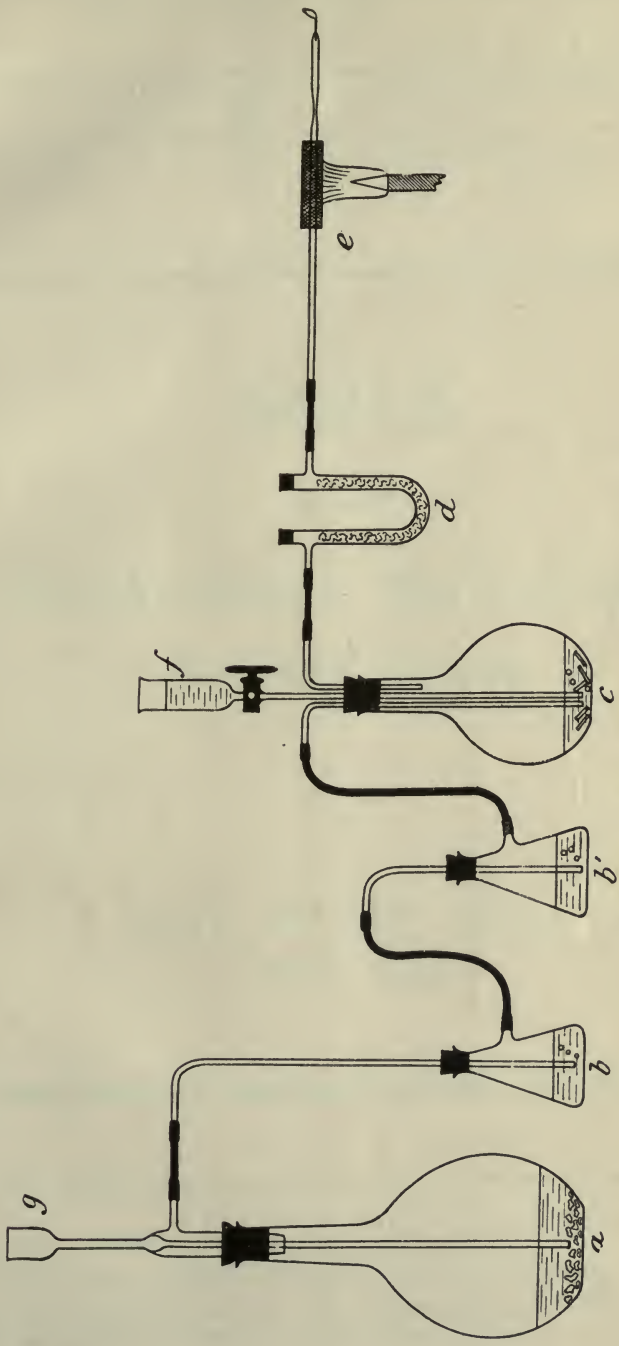
The purified gas now passes into a flask (*c*), holding about 400 cc., the rubber stopper of which has three perforations—one for the inlet tube leading to the bottom of the flask, another for a stoppered funnel tube (*f*), also leading to the bottom, and a third for an exit tube.

A U-tube (*d*), of calcium chloride, is interposed as usual in front of the constricted hard-glass tube (*e*), fitted with platinum jet. The flask (*c*) contains either a few grams of arsenic-free zinc or a bunch of magnesium wire, along with about 20 cc. of water, acidulated with pure H_2SO_4.

To use the apparatus, pour about 50 cc. of 5 per cent. sulphuric acid on to the zinc in the generating flask; then after a couple of minutes the burner under the reduction tube (*e*), which is protected with gauze, is lighted, as well as the gas issuing from the platinum jet.

More acid should be added from time to time, so as to keep the hydrogen flame about 1 cm. in length. If after an hour no mirror is formed, the experiment is again started with further quantities of the same materials, with the exception of the $AgNO_3$ solution, which lasts for a large number of experiments, the stoppered funnel tube (*f*) being filled with the suspected liquid, which is allowed to flow very slowly into the flask (*c*) containing the pure zinc or magnesium.

If arsenic is present, it usually commences to deposit in a few minutes. It is advisable, however, in order to detect very minute quantities, to allow the gas to run a full hour.



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